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# Effect of metal electrodes on the performance of polymer:fullerene bulk heterojunction solar cells

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An increase in the workfunction of the metal top electrode leads to a reduction of the open-circuit voltage, short-circuit current, and power conversion efficiency of organic bulk-heterojunction solar cells. It has been demonstrated that the photocurrent obtained from an active layer comprised of a blend of poly(2-methoxy-5-(3',7'-dimethyloctyloxy)-*p*-phenylene vinylene) (OC<sub>1</sub>C<sub>10</sub>-PPV) and [6,6]-phenyl C<sub>61</sub>-butyric acid methyl ester (PCBM), with lithium fluoride topped aluminum, silver, gold, or palladium electrodes, shows a universal behavior when scaled against the effective voltage across the device. Indeed, model calculations confirm that the dependence of the photocurrent on the effective voltage is responsible for the observed variation in performance of each different electrode. Consequently, for any given metal, only the device's open-circuit voltage is required in order to be able to predict the remaining solar cell parameters. © 2004 American Institute of Physics. [DOI: 10.1063/1.1782252]

Organic photovoltaic devices with active layers comprised of a conjugated polymer and fullerene blend are promising candidates for solar energy conversion.<sup>1</sup> Recent developments such as bulk-heterojunction (BHJ) systems have led to a significant increase in the efficiency of organic solar cells. To date, under AM1.5 illumination, power conversion efficiencies up to 2.5% have been achieved when employing poly(2-methoxy-5-(3',7'-dimethyloctyloxy)-*p*-phenylene vinylene) (OC<sub>1</sub>C<sub>10</sub>-PPV) and the methanofullerene [6,6]-phenyl C<sub>61</sub>-butyric acid methyl ester (PCBM) as the electron donor and electron acceptor, respectively.<sup>2</sup> In addition to attempts to optimize the components and composition of the active layer, modification of the electrodes has led to an improvement of the device performance.<sup>3–5</sup> In recent studies, attention has mainly been focused on the effect of the metal electrodes on the open-circuit voltage ( $V_{OC}$ ) of the cells.<sup>3,4</sup> As such, it has been demonstrated that the  $V_{OC}$  of a cell is governed by the workfunction of the negatively charged electrode, although interface dipoles might complicate this behavior.<sup>4</sup> Conversely, the role of the metal electrodes on other important parameters as the short-circuit current ( $J_{SC}$ ), fill factor (FF), and maximum power point (MPP) has hardly been addressed. However, it has been observed that when employing Al as the top electrode, the insertion of LiF between organic layers and the metal not only enhances the  $V_{OC}$ , as expected from its workfunction, but also increases both the  $J_{SC}$  and FF.<sup>6,7</sup> The origin of this increase, and the resulting 20% enhancement in the efficiency, is less clear. One explanation which has been proposed is that the insertion of a subnanometer LiF layer lowers the series resistance of the device by a factor of 3 or 4, which thereby increases the observed FF.<sup>6</sup> However, it must be stressed that in solar cells the top electrode extracts electrons from the device, in contrast to light-emitting diodes (LEDs) in which charge injection is important.<sup>8</sup> In a recent study, the injection of electrons from various metal electrodes into the lowest unoccupied molecular orbital (LUMO) level of the acceptor

PCBM has been investigated.<sup>4</sup> For electron injection the energy barrier ( $\Phi_B$ ) between the metal electrode and the LUMO level of PCBM is relevant, and has been determined to be 0 eV for LiF/Al (Ohmic contact), 0.65 eV for Ag, 0.76 eV for Au, and 0.94 eV for Pd. The respective processes for the transfer of electrons (injection in LEDs; extraction in solar cells) between PCBM and each metal are schematically represented in Fig. 1. The main distinctions between the two processes are that in the case of extraction, the electrons are not inhibited from leaving the active layer by an energy barrier, and are therefore collected with equal efficiency whatever the electrode. Additionally, since the charge carrier generation process in the PPV/PCBM blend is not affected by the electrodes it is also not obvious why a change in the metal electrode would dramatically affect the series resistance. Recently, we have developed a device model which consistently describes the behavior of PPV/PCBM BHJ solar cells. In this model the photocurrent is dominated by the dissociation efficiency of bound electron-hole pairs at the donor/acceptor interface according to Onsager's theory of geminate charge recombination, which is a field- and temperature-dependent process.<sup>9</sup> In addition, we have investigated the role of various metal electrodes on the performance of polymer/fullerene bulk heterojunction solar cells. We demonstrate that when scaled with the internal electric field, the photocurrent of the cell shows a universal behavior, which proves to be independent of the metal electrode used. The differences in device performance

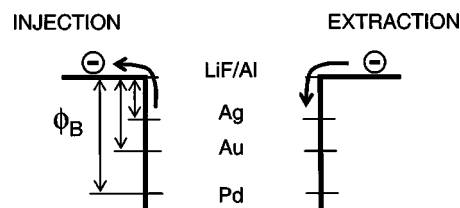


FIG. 1. Schematic energy diagram of an interface between an organic and different top electrodes. The extraction current is independent of the workfunction of the top electrode.

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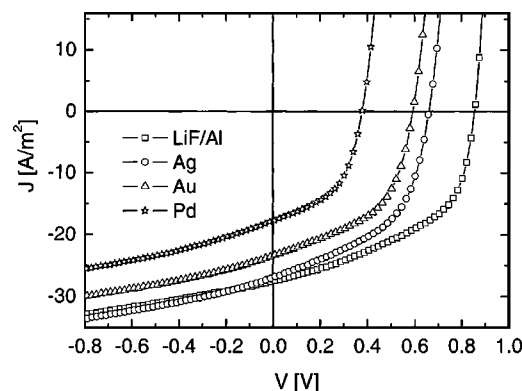


FIG. 2.  $J$ - $V$  characteristics under illumination of an ITO/PEDOT:PSS/OC<sub>1</sub>C<sub>10</sub>-PPV:PCBM 20:80 wt % photovoltaic devices, with LiF/Al, Ag, Au, and Pd as top electrodes (symbols).

between the various metals therefore originates from the change in the electric field in each device, since for each metal a different part of the universal photocurrent-voltage curve is probed. Consequently, once the  $V_{OC}$  has been established for a given metal, the MPP, FF, and  $J_{SC}$  can be directly predicted from our device model.

All devices used during the course of this study were prepared using indium-tin-oxide (ITO) coated glass substrates. To supplement this bottom electrode, a hole transport layer was prepared by first spin coating an aqueous suspension of PEDOT:PSS (Bayer AG) on top of the ITO surface, under ambient conditions, before drying the substrates at 140 °C in an oven. In addition, the active layer was fabricated by spin coating a solution of OC<sub>1</sub>C<sub>10</sub>-PPV and PCBM (1:4 ratio, by weight) in chlorobenzene on top of the PEDOT:PSS coated substrate. To complete the devices, the metal and LiF/metal top electrodes were deposited by thermal evaporation (pressure  $<10^{-6}$  mbar). The respective electrodes and their thicknesses were: gold (Au), 50 nm; palladium (Pd), 50 nm; silver (Ag), 80 nm; lithium fluoride (LiF), 1 nm/aluminum (Al), 100 nm. In order to measure a reliable photocurrent ( $J$ ), the devices were illuminated by a white light halogen lamp with an intensity of 80  $\text{mW/cm}^2$ , under a dry nitrogen atmosphere. A determination of the net photocurrent ( $J_{ph}$ ) was made by also recording the current density in the dark and subtracting it from the photocurrent, and the  $V_{OC}$  was determined from the resulting  $J_{ph}$ - $V$  curve.

The experimentally determined photocurrent-voltage ( $J$ - $V$ ) characteristics of ITO/PEDOT:PSS/OC<sub>1</sub>C<sub>10</sub>-PPV:PCBM/cathode (cathode=LiF/Al, Ag, Au, Pd) devices are illustrated in Fig. 2. The  $V_{OC}$  of these devices after correction for the dark current are: LiF/Al=0.90 V; Ag=0.70 V; Au=0.59 V; Pd=0.40 V, respectively. The  $J_{SC}$  decreases from 28  $\text{A/m}^2$  for LiF/Al to only 17  $\text{A/m}^2$  for Pd. Although the experimental data in Fig. 2 are measured at the same light intensity, a difference in the reflectivity and/or interface roughness of the top electrode materials means that the quantity of photons absorbed by the active layer is almost certainly not equal,<sup>10</sup> thus resulting in a slight variation in the photocurrent. In the case of Au and Pd, the higher surface reflectivity means that the photocurrent is typically 11% less than that of Ag and LiF/Al. In a previous report, we were able to show that when subjected to a large reverse bias ( $\geq -10$  V) the photocurrent saturates and becomes voltage and temperature independent.<sup>9</sup> This implies that all photogeneration

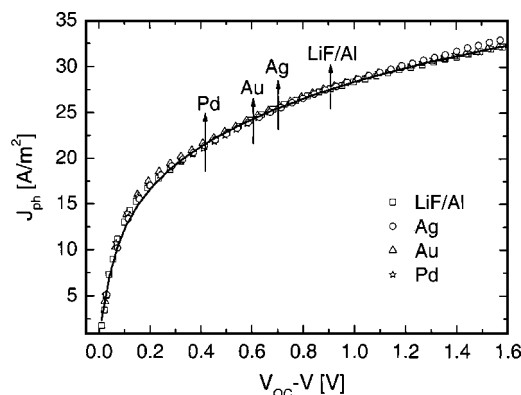


FIG. 3. Photocurrent vs effective applied voltage ( $V_{OC}-V$ ) of an OC<sub>1</sub>C<sub>10</sub>-PPV:PCBM device for four different top electrodes (symbols), at 295 K. The solid line represents the numerical calculation, and the arrows indicate the short-circuit current densities ( $V=0$  V) and corresponding open-circuit voltages of these devices.

ated charge carriers are extracted from the active layer before recombining, and that their rate of generation approaches the maximum possible. The existence of such a saturated photocurrent allows us to correct the experimental data for the maximum generation rate, which subsequently more correctly reflects the number of photons absorbed by the active layer for the data presented. The corrected  $J_{ph}$ - $V$  characteristics are plotted against  $V_{OC}-V$  in Fig. 3, which reflects the internal electric field in the device, together with the model calculations. In all cases, the individual curves coincide with one universal curve, demonstrating that, as expected, the photogeneration processes in the photoactive layer are not dependent on the nature of the top electrode. Moreover, it shows that no additional contact resistance is induced when the top contact is changed from Ohmic (LiF/Al) to non-Ohmic (Ag, Au, Pd) as depicted by Fig. 1. With a change in the top electrode the  $V_{OC}$  is affected due to modification of the metal workfunction. The reason for the observed changes in  $J_{SC}$ , FF, and MPP is now clear from Fig. 3: the voltage area between the origin ( $V=V_{OC}$ ) and the arrow ( $V=0$  V) reflects the active (fourth quadrant) part of the device for each top electrode. Consequently, a different region of the  $J_{ph}$ - $(V_{OC}-V)$  curve shown in Fig. 3 is probed when  $V_{OC}$  is modified. The dependence of the photocurrent on the effective voltage ( $V_{OC}-V$ ) or field in the device being responsible for the observed changes of  $J_{SC}$ , FF, and MPP.

We recently addressed the relationship, and ultimate dependence, of the photocurrent of devices with LiF/Al top electrodes on temperature—and the applied voltage.<sup>9</sup> The device model solves numerically the Poisson equation, continuity equations, and current equations including both drift and diffusion. A similar model has been presented by Barker *et al.*<sup>11</sup> for bilayer devices. As shown in Fig. 3 these model calculations describing the photocurrent of PPV:PCBM BHJ solar cells are in excellent agreement with the experimental photocurrents. For electrodes in which the Fermi level aligns as expected according to their workfunction, such as silver, the  $V_{OC}$  of the solar cell can be directly calculated.<sup>4</sup> Consequently, for these electrodes only knowledge about their workfunction is required to predict the  $J_{SC}$ , FF, and MPP. However, this is not the case when considering gold electrodes, in which interface dipoles are known to play a role.<sup>4</sup> Accordingly, there is not a direct linear correlation between the  $V_{OC}$  and the metal's workfunction, and therefore  $V_{OC}$  has

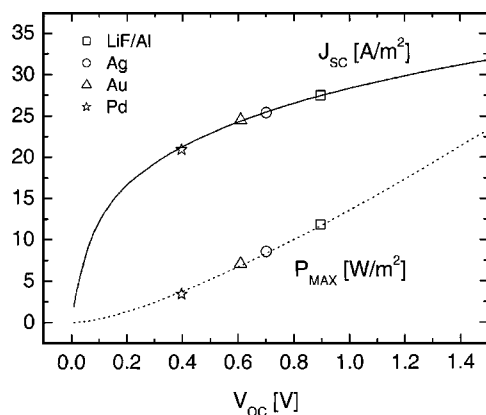


FIG. 4. Experimental short-circuit current  $J_{SC}$  and the maximum output power  $P_{max}$  as a function of  $V_{OC}$  (symbols) for four different electrodes at 295 K. The solid and dotted lines represent the numerical calculation for  $J_{SC}$  and  $P_{max}$ , respectively.

to be measured. The experimentally determined  $J_{SC}$  and maximum output power ( $P_{max}$ ) values as a function of  $V_{OC}$  (symbols; calculated values, lines), at 295 K, for four different electrodes are shown in Fig. 4. In each instance, the device thickness totaled 95 nm. The increase in  $P_{max}$  with increasing  $V_{OC}$  reflects the movement of the MPP along the  $J_{ph}-(V_{OC}-V)$  curve of Fig. 3. Furthermore, from considering Fig. 4 it is also possible to determine exactly how much the power conversion efficiency will rise when the  $V_{OC}$  itself is increased, as would occur with a shift in the PCBM LUMO level.

In conclusion, we have been able to demonstrate that the photocurrent in BHJ solar cells is not affected by varying the negatively charged metallic top electrode when scaled

against the effective voltage over the device. In addition, the dependence of the photocurrent on the effective voltage is responsible for the difference in performance of the various top electrodes. Moreover, model calculations demonstrate that all of the applicable device parameters can readily be elucidated once the open-circuit voltage is known.

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